#### (19) World Intellectual Property Organization

International Bureau





(43) International Publication Date 8 July 2004 (08.07.2004)

PCT

## (10) International Publication Number WO 2004/057171 A1

(51) International Patent Classification<sup>7</sup>: 9/20, 9/28, F23R 3/40

F02C 9/18,

(21) International Application Number:

PCT/EP2003/014563

(22) International Filing Date:

12 December 2003 (12.12.2003)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: MI2002A002757

23 December 2002 (23.12.2002) I'

- (71) Applicant (for all designated States except US): NUOVO PIGNONE HOLDING S.P.A. [IT/IT]; Via F. Matteucci, 2, I-50127 Firenze (IT).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): FECAMP, Benoit [FR/IT]; Via ponte alle Mosse 32, I-50144 Firenze (IT). FADLUN Ever, Avriel [IT/IT]; Piazzale dei Caduti della Montagnola 72, I-00142 Roma (IT). GROPPI, Stefano

[IT/IT]; Piazza del Popolo 27, I-51015 Monsummano Terme (Pistoia) (IT).

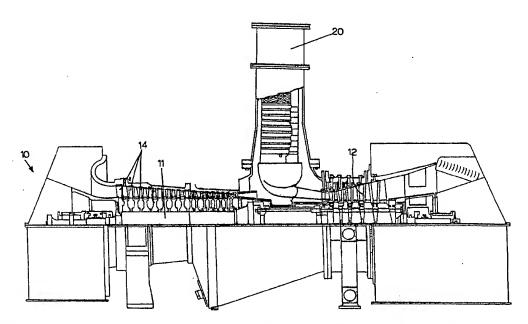
- (74) Agents: COPPO, Alessandro et al.; Ing. Barzanò & Zanardo Milano S.p.A., Via Borgonuovo, 10, I-20121 Milan (IT).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### Published:

with international search report

[Continued on next page]

(54) Title: SYSTEM FOR CONTROLLING AND OPTIMIZING THE EMISSION OF A CATALYTIC COMBUSTOR IN A SINGLE-SHAFT GAS TURBINE



(57) Abstract: System for controlling and optimizing the emissions of a catalytic combustor in a single-shaft gas turbine (10), comprising at least one calculation unit for implementing a mathematical model of the operation of the said gas turbine (10), on the basis of a set of predetermined parameters, by means of which the aforesaid emissions can be optimized during variations of the operating conditions of the turbine over a range of external environmental conditions from approximately -29°C to +49°C.

### WO 2004/057171 A1



 before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

SYSTEM FOR CONTROLLING AND OPTIMIZING THE EMISSIONS OF A CATALYTIC COMBUSTOR IN A SINGLE-SHAFT GAS TURBINE

The present invention relates to a system for controlling and optimizing the emissions of a catalytic combustor in a single-shaft gas turbine.

A gas turbine is defined as a rotating thermal machine assembly which converts the enthalpy of a gas to useful work, using gas obtained directly from a combustion process, and supplying mechanical power on a rotating shaft.

10

15

20

A turbine therefore usually comprises a compressor, most commonly of the axial type, outside a combustion chamber and a turbine (turboexpander) which, in a single-shaft gas turbine, supplies both energy for moving the compressor and power to the user.

The turboexpander, the compressor, the combustion chamber, the mechanical energy output shaft, the control system and the starting system form the essential parts of a gas turbine.

As regards the operation of a gas turbine, it is known that the fluid passes into the compressor at low pressure and at low temperature; in flowing through the

WO 2004/057171

4/ pols

PCT/EP2003/014563

## JC20 Rec'd PCT/PTO 2 2 JUN 2005.

compressor, the gas is compressed and its temperature rises.

The gas then enters the combustion chamber, where it undergoes a further significant temperature increase.

Thus the enthalpy of the gas can be exploited to obtain useful work; this is because the work given up by the gas to the turbine is greater than that absorbed by the compressor, and therefore a certain amount of energy remains available on the shaft of the machine, and this energy, after subtraction of the work absorbed by the accessories and by the passive resistance of the moving mechanical members, constitutes the useful work of the system.

15 At the outlet of the combustion chamber, therefore, the gas, at high pressure and high temperature, passes through suitable pipes and reaches the turbine, where it gives up some of the energy accumulated in the compressor and in the combustion chamber and then flows to the outside through the exhaust pipes.

In the last few decades, the problem of environmental pollution has led to the introduction of various laws designed to regulate the emission of pollutants to the

atmosphere, in an attempt to make air quality acceptable.

Consequently, national and international standards require the use of methods and equipment for reducing the pollutants present in gases, these methods and equipment being suitably designed according to the chemical and physical properties of the gases.

5

10

15

20

In general, the emissions of gas turbines comprise various chemical species which have been fully oxidized or which do not tend to react, principally  $CO_2$ ,  $H_2O$ ,  $N_2$  and  $O_2$ ; species with a low level of oxidation, such as CO, unburnt hydrocarbons, particulates, and mixtures of nitrogen and sulphur oxides denoted  $NO_x$  and  $SO_x$  respectively, are also present in the emissions as pollutants in concentrations of the order of parts per million (ppm).

As regards the fully oxidized species and nitrogen, the content of these in emissions can be calculated provided that the composition of the fuel used and the operating conditions of the machine are known.

As regards the other pollutants, however, it is practically impossible to evaluate their concentration, except in the case of total sulphur oxides.

Therefore, in order to determine the values of these pollutants (CO, unburnt hydrocarbons, particulates,  $SO_x$  and  $NO_x$ ) it is necessary to make accurate measurements and conduct theoretical analyses.

- 5 Unburnt hydrocarbons are generally present as a result of inefficient combustion which does not fully oxidize the combustible species present, but their presence is limited to a few ppm and therefore does not constitute a significant pollution problem.
- As regards the sulphur oxides, these consist of a mixture, in variable proportions, of  $SO_2$  and  $SO_3$  which combine with water vapour to form the corresponding acids.
- Sulphur oxides are practically absent from combustion

  15 fumes caused by burning natural gas, and as a general

  rule their formation is prevented by selecting the

  fuels, opting for those with a very low sulphur

  content.
- For nitrogen oxides  $(NO_x)$  and carbon monoxide (CO), the picture is much more complicated; in order to control these substances, particular attention must be paid to the gas combustion temperature.

For example, in the case of nitrogen oxides (generally

denoted  $NO_x$ ), their presence in emissions decreases rapidly as the combustion temperature is reduced.

Conventional technologies for reducing these pollutants, such as water and water vapour injection, cannot achieve the extremely low emission levels required by the law in force in many areas.

 $NO_{\mathbf{x}}$  is produced in three main ways during the combustion process:

- by reaction with  $N_2$  in combustion with oxygen at high temperatures;
  - from the nitrogen present in fuels;
  - by the reaction of the radical derivatives of fuels, such as  $N_2$  converted to NO.

The formation mechanism must be known to enable the  $NO_x$  emission to be controlled efficiently.

The simplest and most widely used model of  $NO_{x}$  formation is that discovered by Zeldovich, which uses the following reactions:

$$N_2 + O \rightarrow NO + N$$

$$O_2 + N \rightarrow NO + O$$

5

$$OH + N \rightarrow NO + H$$

These reactions are independent of the type of combustion used for the reaction, since they take place

at the high temperatures developed by the reagents themselves.

The formation of  $NO_x$  can be controlled by modifying the operating conditions during the combustion process.

5 For example, the quantity of oxygen present can be reduced to minimize the formation of NO<sub>x</sub>. In practical terms, a small quantity of air is used; the introduction of water into furnaces reduces the temperature as a result of the energy jump caused by the latent heat of the water.

A reduction technology used at present is selective catalytic reduction (SCR), in which ammonia is used together with the catalytic process.

The ammonia is injected with the burnt gases into the catalysis bed. The nitrogen oxides  $NO_x$  are combined with the ammonia on the surface of the catalyst and are dissolved in water and nitrogen.

This system has proved to be advantageous for eliminating  $NO_x$ , but its costs are high.

A different approach to nitrogen oxide reduction makes use of a catalytic post-combustion process, with a platinum catalyst and a nitrogen oxide removal agent consisting of potassium carbonate.

Both of the aforesaid technologies, although of proven validity in terms of the reduction of nitrogen oxide concentration achieved, are of little practical use because of the significant loss of efficiency which they cause in the turbine.

5

Furthermore, all the technologies used up to the present time are highly sensitive to the variation of operating conditions, particularly the ambient temperature and the required load.

Combustion by means of a catalytic combustion chamber resolves the problems of cost and complexity inherent in the solutions described above for reducing pollutants ( $NO_x$  and CO).

The object of the present invention is to provide a system for controlling and optimizing the emissions of a catalytic combustor, which makes it possible to reduce the concentration of pollutants such as nitrogen oxides ( $NO_x$ ) and carbon monoxide to values close to zero ppm over a wide operating range of a gas turbine.

20 Another significant object of the invention is to provide a system for controlling and optimizing the emissions of a catalytic combustor in a gas turbine which can be implemented with production and

maintenance costs which are relatively low in view of the advantages obtained.

These and other objects of the present invention are achieved by providing a system for controlling and optimizing the emissions of a gas turbine of the type comprising a catalytic combustor, and comprising at least one calculation unit for implementing a mathematical model of the operation of the said gas turbine, on the basis of a set of predetermined parameters, by means of which the aforesaid emissions can be optimized during variations of the operating conditions of the turbine over a wide range of external environmental conditions, as disclosed in Claim 1.

5

10

15

20

Further detailed technical characteristics are specified in the subsequent claims.

In particular, the control system according to the present invention makes it possible to limit the incidence of the phenomenon in which, during load variations, there is an abrupt rise in the flame temperature in the precombustor and a consequent concentration of pollutants such as nitrogen oxides well above the permitted limit values.

The characteristics and advantages of a system for controlling and optimizing the emissions of a catalytic

combustor in a gas turbine according to the present invention will be made clearer by the following description, provided by way of example and without restrictive intent, which refers to the attached schematic drawings in which:

- Figure 1 is a schematic lateral view of a gas turbine according to the invention;
- Figures 2 to 4 show diagrams representing the control parameters for the operation of the turbine;

5

20

- Figure 5 is a block diagram illustrating a detail of the operation of the system according to the invention.

With particular reference to Figure 1, a gas turbine 10

15 essentially comprises an axial compressor 11, a

combustor 20, and a turbine 12.

In the illustrated example, the combustor 20 has a head, immediately downstream of which there is a first combustion region followed by a catalytic cell and a post-combustion region.

This combustor 20 is designed to be supplied with gas fuels.

An array of adjustable vanes 14, also known by the acronym IGV ("Inlet Guide Vanes"), can be seen at the

inlet of the compressor 11.

5

10

15

The adjustable vanes (IGV) can be adjusted and/or rotated in order to set them at an appropriate angle to the direction of the air entering the compressor, in such a way as to vary the flow rate at the turbine inlet.

To control the adjustable vanes (IGV), the positions of the vanes 14 of the distributors must be made dependent adjustment of the turbine exhaust on the temperature, the turbine speed, the compressor exhaust pressure and the air temperature at the turbine inlet, in such a way as to keep the turbine operating conditions within an operating region A in which the unburnt carbon monoxide and of concentrations substances in the exhaust gases are minimized in all technologically possible operating conditions in a temperatures varying ambient range of approximately -29°C to +49°C and over a wide power range.

The control system for the adjustable vanes (IGV) described above is associated with a system for bleeding hot air from the compressor exhaust (known as an IBH, an acronym for "inlet bleed heating system") for keeping the compressor exhaust, which is introduced

into the inlet of the compressor, in standard (ISO) conditions.

The bleed system (IBH) is controlled by programming the opening of the valve in accordance with the angle of rotation of the adjustable vanes (IGV).

5

10

The combined effect of the rotation of the adjustable vanes (IGV) and the bleed system (IBH) makes it possible to control the variation of the difference between the gas temperature at the exhaust of the first combustion region (TPBEX) and the compressor exhaust temperature  $(T_3)$ .

This variable is also denoted by the term Trise (Trise = TPBEX - T<sub>3</sub>).

Trise has to be kept within certain limits, because 15 most of the  $NO_{\rm x}$  is produced in this first combustion region and is a function of the increase in Trise.

TPBEX, and consequently Trise, are also decreasing functions of the adiabatic temperature  $(T_{ad})$  at the catalyser outlet from the combustion chamber.

In order to keep TPBEX low (for low  $NO_x$  production) it is therefore necessary to maximize  $T_{ad}$  (where  $T_{ad}$  is defined as the temperature which would be present at the outlet of the combustion chamber if combustion were complete).

The trend of the variation of the adjustable vanes (IGV) with respect to ISO standard conditions is linear, and remains constant up to a certain value of CPR (the compressor pressure ratio, defined as the ratio between the total pressure of the air leaving the compressor and the pressure of the incoming air), and then decreases in a linear way.

5

10

15

20

The correlation between the flow rates produced by the bleed system (IBH) and the angular rotation of the adjustable vanes (IGV) to keep T<sub>3</sub> constant over a wide ambient temperature range varying from approximately -29°C to approximately +49°C is summarized in Figure 4, which shows the trend of the flow rates of the bleed system (IBH) on the vertical axis as functions of the angle of rotation of the adjustable vanes (IGV) (on the horizontal axis).

The diagram in Figure 4 shows a set of curves having substantially linear trends, corresponding to the different loads required by the machine, in particular a first curve 41 representing ISO T<sub>3</sub>, a second curve 42 expressing the trend of the bleed system (IBH) at 50% power, a third curve 43 at 60%, a curve 44 at 70%, and a curve 45 at 80%.

In practice, when increasing or decreasing the supply of fuel, in other words when requesting more or less power, it is necessary to carry out the adjustments while maintaining these relations between the characteristic values of the bleed system (IBH) and the rotation of the adjustable vanes (IGV), in order to keep a constant temperature T<sub>3</sub> for a given ambient temperature.

With reference to Figure 2, this shows a diagram in

which the inlet temperature of the catalyser TIC is
shown on the vertical axis and the fuel-air composition
ratio F/A is shown on the horizontal axis.

15

20

The operating region A in which it is necessary to act optimize the reduction order to in concentrations of nitrogen oxides, carbon oxide and unburnt hydrocarbons in the emissions is delimited by a lower line 50 which defines the catalyst activation temperature, a curve 51 positioned towards what are known as lean mixtures, in other words those with a low fuel value, representing the limit for the production of carbon monoxide at the various temperatures, and a pair of upper curves 52 and 53 which represent the limit temperatures for the catalyst, the first upper curve 52 relating to lean mixtures and the second curve

53 relating to rich mixtures, in other words those with a high fuel content.

Within the region A the number 54 indicates the recommended optimal starting point for the operations, while the arrows U indicate the path to be followed when the power of the gas turbine is to be reduced, in other words when less fuel is introduced.

5

10

15

20

Figure 3 illustrates the principle expressed above in a different context, in other words as a correlation of the trend of TPBEX (vertical axis) as a function of the temperature of the catalyst  $T_{ad}$  (horizontal axis).

Thus, when the load of the gas turbine with a catalytic combustion chamber is reduced (so that  $T_{ad}$  falls), the temperature TPBEX must be increased to maintain the correct operation of the catalyst.

As stated previously, the emission of nitrogen oxide is an increasing function of Trise (TPBEX and  $T_3$ ), and therefore, when the load is reduced, it is necessary to compensate for the normal lowering of  $T_3$  and the increase in the TPBEX requirement, as the latter effect would cause an excessive increase in  $NO_x$ .

In practical terms, if the emissions are to be optimized the machine must operate in the conditions defined by the curve, and the bleed system (IBH) must

be operated at all times so that this curve is followed.

The operating procedures are constrained by the ranges of values within which the machine operates, namely a rotation of the adjustable vanes (IGV) between 0 and - 50 degrees, and a flow rate of between 0 and 5% of W2 for the bleed system (IBH), where W2 denotes the flow rate of the air drawn in by the compressor.

5

15

The required results are a power level meeting ISO standards, a reduction of NO<sub>x</sub> from 50% to 100% from -29°C to 49°C, and a reduction of carbon monoxide, CO, from 50% to 100% from -29°C to 49°C.

The adjustments made possible by the invention enable the maximum standard flow rate according to ISO standards to be modified by a rotation of the adjustable vanes (IGV) equal to 0, while the flow rate of the bleed system (IBH) varies from 0 to 100% of load according to ISO standards.

With reference to the diagram of Figure 5, a

20 mathematical model of the operation of the said gas
turbine 10 is implemented in the calculation unit 60,
on the basis of a set of predetermined parameters and
as a function of data measured in the gas turbine, in
such a way as to optimize the aforesaid emissions

during variations of the operating conditions of the turbine over a range of external environmental conditions extending from approximately -29°C to +49°C.

In practice, the parameter on which the calculation unit 60 operates is the adjustment of the extraction flow rate of the bleed system (IBH), based on the measurement of the angle of rotation of the distributor vanes (IGV) 14 and the ambient temperature 63.

5

15

20

For greater accuracy, the calculation unit 60 will also be designed to allow for the compressor inlet pressure 61 and the absolute humidity at the compressor inlet 62.

Thus the implementation of the control system as described makes it possible to obtain an excellent result in terms of optimal control, good performance being established by maintaining the flame temperature in the precombustor below the specified limits and thus below the pollutant emission level, in both transient and regular operating conditions, as predicted by simulations which have been conducted.

The above description clearly demonstrates the characteristics of the system for controlling and optimizing the emissions of a catalytic combustor in a single-shaft gas turbine, which forms the object of

the present invention, and also makes clear the advantages of the system, which include:

- reduced levels of polluting emissions;
- reduced pressure oscillations in the combustion chamber and good flame stability;
- high combustion efficiency;

- simple and reliable operation;
- relatively low production and maintenance costs by comparison with the prior art;
- 10 a calculated flame temperature in the precombustor held below predetermined limit values.

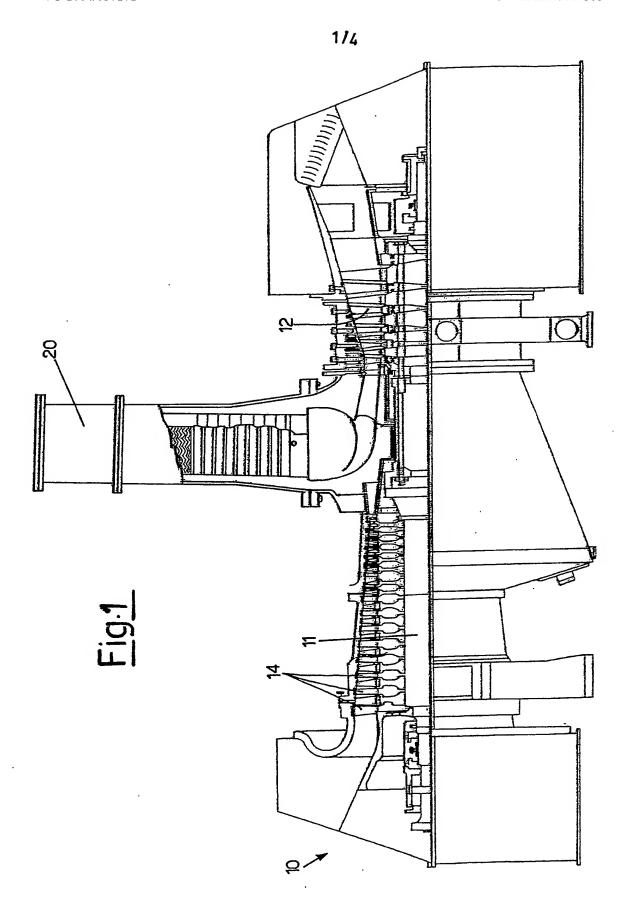
#### CLAIMS

- 1. System for controlling and optimizing the emissions of a catalytic combustor in a gas turbine (10), comprising at least one calculation unit (60) for implementing a mathematical model of the operation of the said gas turbine (10), on the basis of a set of predetermined parameters, by means of which the aforesaid emissions can be optimized during variations of the operating conditions of the turbine over a range of external environmental conditions from approximately -29°C to +49°C.
- Control and optimization system according to Claim 1, in which the parameters on which the said calculation unit (60) operates comprise an adjustment of the flow rate of a bleed system (IBH) as a function of the ambient temperature (63) and of the rotation of the adjustable vanes (IGV) (14).
- 20 3. Control and optimization system according to Claim 2, in which the input parameters of the said calculation unit (60) additionally include the compressor inlet pressure and the absolute

humidity at the compressor inlet, in order to provide greater accuracy.

4. Control and optimization system according to Claim 2, in which the values of the parameters on which the said calculation unit (60) operates are in the range from 0 to -50 degrees for the rotation of the adjustable vanes (IGV) (14) and in the range from 0 to 5% of the flow rate (W2) for the bleed system (IBH), where (W2) is the flow rate of air drawn in by the compressor.

5





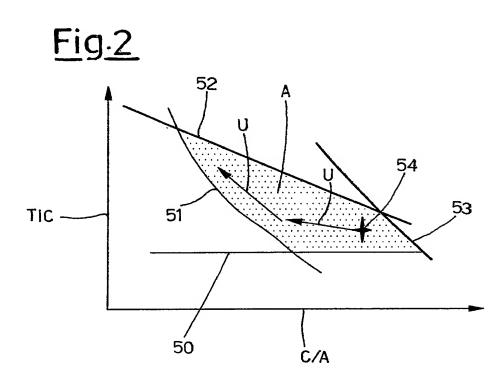
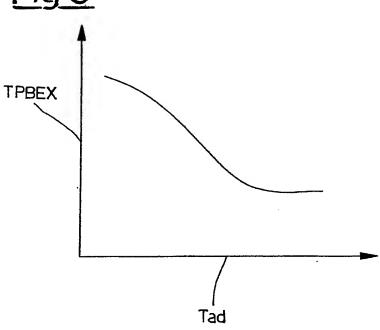
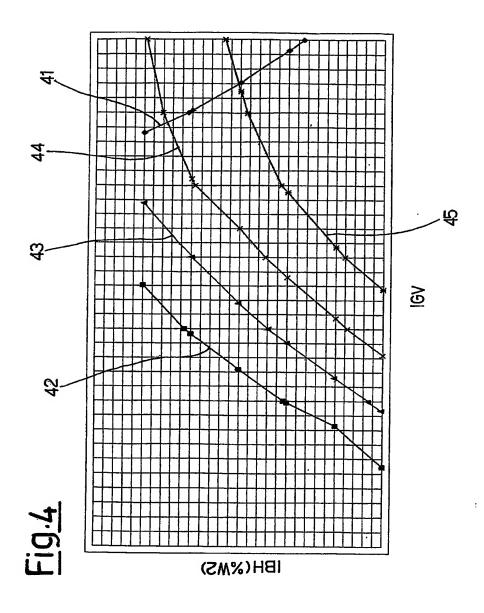


Fig.3



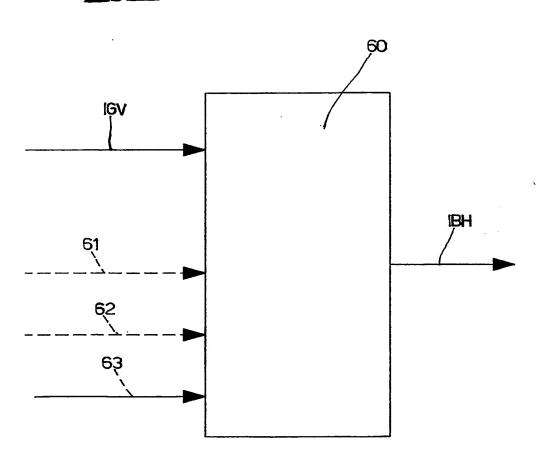
3/4



PCT/EP2003/014563

4/4

Fig.5



### INTERNATIONAL SEARCH REPORT

national Application No PCT/EP 03/14563

CLASSIFICATION OF SUBJECT MATTER PC 7 F02C9/18 F02C F02C9/20 F02C9/28 F23R3/40 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 - F02C - F23RDocumentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, WPI Data C. DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No. Category ° Citation of document, with indication, where appropriate, of the relevant passages 1 X US 6 095 793 A (GREEB KEVIN) 1 August 2000 (2000-08-01) Y the whole document 2,3 DE 101 34 612 A (ALSTOM SWITZERLAND LTD) 1 X 5 September 2002 (2002-09-05) column 1, line 29 - line 37 column 2, line 32 paragraph '0022! US 4 733 527 A (KIDD HARRY A) 1 X 29 March 1988 (1988-03-29) column 1, line 6 - line 13 column 2, line 41 - line 44 claim 2 Further documents are listed in the continuation of box C. Patent family members are listed in annex. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance invention 'E' earlier document but published on or after the international filing date \*X\* document of particular relevance; the claimed Invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. 'O' document referring to an oral disclosure, use, exhibition or document published prior to the International filing date but later than the priority date claimed \*&\* document member of the same patent family Date of mailing of the international search report Date of the actual completion of the international search 28 April 2004 11/05/2004 Authorized officer Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo n), Fax: (+31-70) 340-3016 Steinhauser, U

### INTERNATIONAL SEARCH REPORT

PCT/EP 03/14563

		101/21 03/14503
	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category *	Citation of document, with Indication, where appropriate, of the relevant passages	Relevant to claim No.
Х	US 2002/083715 A1 (DALLA BETTA RALPH A ET AL) 4 July 2002 (2002-07-04) claim 9	. 1
X	US 2002/029557 A1 (TOBO MASAYUKI ET AL) 14 March 2002 (2002-03-14) paragraph '0058! paragraph '0061!	1
Y	US 5 168 447 A (MOORE LELAND E) 1 December 1992 (1992-12-01) column 4, line 9 - line 25 column 7, line 5 - line 25	2,3
<b>A</b>	US 5 174 105 A (HINES WILLIAM R) 29 December 1992 (1992-12-29) column 5, line 29 - line 47 column 6, line 1 - line 11 column 6, line 38 - line 51	2
Α	PATENT ABSTRACTS OF JAPAN vol. 017, no. 306 (M-1428), 11 June 1993 (1993-06-11) -& JP 05 026057 A (HITACHI LTD), 2 February 1993 (1993-02-02) abstract	2
A	US 6 364 602 B1 (COTRONEO JOSEPH A ET AL) 2 April 2002 (2002-04-02) column 5, line 15 - line 33	1-4

# INTERNATIONAL SEARCH REPORT Information on patent family members

national Application No									
PCT/EP	03/14563								

					•	•
Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 6095793	Α	01-08-2000	AU CA EP JP WO	6151099 2344210 1114279 2002525490 0017577	A1 A1 T	10-04-2000 30-03-2000 11-07-2001 13-08-2002 30-03-2000
DE 10134612	Α	05-09-2002	DE EP JP US	10134612 1234962 2002266658 2002178731	A2 A	05-09-2002 28-08-2002 18-09-2002 05-12-2002
US 4733527	Α	29-03-1988	NONE			
US 2002083715	A1	04-07-2002	EP WO	1334307 02073090		13-08-2003 19-09-2002
US 2002029557	A1	14-03-2002	JP DE FR	2002070584 10142514 2813342	A1	08-03-2002 13-06-2002 01-03-2002
US 5168447	Α	01-12-1992	NONE			
US 5174105	Α	29-12-1992	GB	2251657	A ,B	15-07-1992
JP 05026057	Α	02-02-1993	JP	2954754	B2	27-09-1999
US 6364602	B1	02-04-2002	NONE			